

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant: Jetten et al.

Serial No.: 10/519,639

Filed: February 8, 2006 (International filing: June 23, 2003)

Title: Process for Cleaning Filters

Group: 1792

Examiner: S.T. Chaudhry

July 7, 2010

DECLARATION UNDER 37 CFR SECTION 132

Hon. Commissioner of Patents
and Trademarks
Washington, D.C. 20231

Sir:

I, Jan Matthijs Jetten, residing at Costerlaan 3B, 3701 JL Zeist, The Netherlands, do hereby declare that:

1. I am a citizen of the Netherlands,
2. I have an educational and technical background in the field of Analytical and Organic Chemistry:
 - a) I am a Ph.D. graduate from the Technical University of Delft, The Netherlands, 2003, on a thesis entitled "Tempo-mediated cleaning of membranes for beer clarification and surface water treatment";
 - b) I was employed by TNO Nutrition from 1988 until 2000 as a research engineer and a project leader involved in food production processes;

c) From 2004, I was employed by TNO Nutrition, as a project leader and team leader in the field of innovative ingredients and processes, in the field of industrial biopolymers, and, since 2008, in the field of functional ingredients;

3. I am familiar with Jetten et al., US application 10/519,639 filed February 8, 2003, of which am a named inventor;
4. I am familiar with Mol et al., PCT patent application WO 97/45523 and US 6,274,186, the teachings of which I see as the same;
5. I have read Jennings et al. US 3,912,624, and Fremont et al., US 4,740,308; I have also read Schuchardt, US 4,970,005.
6. I declare the following with regard to the problems related to filtering beverages in general and beer in particular, and to the maintenance and cleaning of such filters, in the light of the teachings of Mol et al; Jennings et al; and Fremont et al.
7. Around 1999, we set out to find a process and means for cleaning polymer membrane filters used in the beer-brewing and related industry. The purpose of these filters is to remove poorly water-soluble materials such as yeast material, proteins, polysaccharides including celluloses and other β -glucans, and polyphenols, from the liquid stream. However, these materials have a tendency to aggregate, and to limit the flux rate through the filter and retain materials that normally permeate through the filter; eventually the filter is blocked after relatively short periods.
8. We were aware of several methods for cleaning such blocked filters, as described in the introductory part of the present application. We were familiar with the teaching of Mol et al., who dealt with essentially the same problem. Mol et al., after reviewing the various alternatives, recommend to clean the fouled filters by circulating solutions of high concentration of hypochlorous acid (4.5 g/l = about 4500 ppm) in the presence of bromide and TEMPO (see Example 1 of Mol et al.). TEMPO is a known oxidation catalyst and is used in Mol et al. in this capacity. Having extensive experience with TEMPO-mediated oxidation ourselves, we were confident that such treatment could be effective to a reasonable extent, but we were concerned that the high levels of chlorine and bromine had the risk of leaving chlorinated and brominated residues in the filter, which may conflict with safety provisions for food processes. Moreover, TEMPO is a nitroxide, and although not known for being a serious health hazard, it is not generally accepted in the food and beverage industry.

9. When looking for alternatives for the TEMPO-catalyzed bromide/hypochlorite oxidation of Mol et al., we noted that Mol et al. reported that the oxidation with non-catalyzed hypochlorite or hypobromite or with peroxide/metal complexes was unsatisfactory, since these agents would not allow to attain the original flux rates. In view of this teaching away, we initially focused on oxidizing agents not mentioned by Mol et al., such as peroxydisulfate and complex persulfates (Oxone). Although acceptable cleaning performances were achieved with these agents, flux rates after cleaning were not fully satisfactory. Some of these results are reported in the present application, Examples 1.3 and 1.5. In a further investigation, these agents were tested in a back-flush mode, with only a slight improvement in cleaned flux rate; see Examples 2.1, 2.2, 2.5, 2.6 and 2.7. Non-catalyzed hydrogen peroxide gave a moderate further flux increase (Examples 2.8 and 2.9).
10. We then performed a cleaning test using just hypohalous acid, without catalyst, and found surprisingly high cleaned flux rates; see Examples 1.1, 1.2, 2.3 and 2.4. These fluxes were especially high in the back-flush mode using relatively low pH values: see Example 3.5 showing a flux rate of the same order (62 and 72 ml/s) as the original flux of 70 ml/s). This surprising result led us to proceed against the teaching Mol et al. altogether, and we found similarly high cleaned flux rates when using metal/peroxide oxidation: see Examples 3.1-3.4, 4.2 and 4.3. The high fluxes were also attained when using direct oxidant concentrations that were significantly below those of Mol et al., 2000-3000 ppm vs. 4500 ppm; see Examples 2.3, 2.4, 3.2, 3.4, 3.5. We never expected such results with a TEMPO-free process on the basis of the teaching of Mol et al.
11. In our research, we did not take into account the teaching of Jennings et al. Jennings et al. do not appear to be concerned with the problems we were faced with, i.e. the cleaning of filters in the brewing and related industry, but instead with reversed osmosis and ultrafiltration, where the problems are remote from those of filtering beer liquids. Reversed osmosis and ultrafiltration are unsuitable for the filtration of beer, since these techniques would result in the loss of valuable components such as certain proteins and affect oxygen uptake. Jennings et al. give a survey of various cleaning techniques, and conclude that such techniques are disadvantageous as these are time consuming and use liquid streams (col. 1, lines 35-62). As the system promoted by Jennings et al. uses pressurized air-carrying droplets, it is not suitable for cleaning polymer membranes used for beverages in our systems. I do not see how, even with the knowledge of today, Jennings et al. could have put us on the track of the instantly claimed process. Where Jennings et al. refer to molds and bacteria as materials to be removed in the food dairy industry (col. 1, lines 31-38), these are not relevant for our problem of filtering beer and other beverages. In filtering beer, the so-called 'cold drip', is the most important contamination apart from yeast cells. The cold drip is formed by crystallization of complexes of

otherwise soluble or dispersible polyphenols and proteins at the low lager temperatures of e.g. 2-4°C (35-40°F), wherein the polyphenols adhere to the membranes by covalent interaction. So the nature of the contaminating materials to be treated in our process is very different from those referred to by Jennings et al. and we would not expect the review by Jennings et al. to work for our problem.

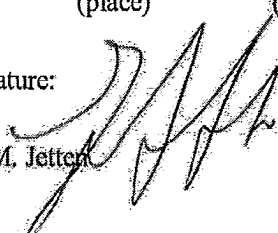
12. Fremont et al. report the cleaning of ultrafiltration membranes. Ultrafiltration membranes are not suitable for filtering beer and other beverages, as explained above. Fremont et al. have studied various conventional cleaning agents, and found that they do not work satisfactorily. Among these unsatisfactory agents is 4.1% (= 41,000 ppm) acidic hydrogen peroxide (Comparative Example 8, Table I). The agents that do work according to Fremont et al. are highly concentrated (7.5% - 30%) hydrogen peroxide followed by concentrated (5.25%) hypochlorite (Examples 1-3). Such high concentrations are prohibitive for cleaning in the beverage and beer brewing industry, because of the high cost and high volumes of water need for rinsing, and because of the shortened life of the membranes themselves as most synthetic membranes are sensitive to such oxidizing agents. Therefore, I do not consider the teaching of Fremont et al. as overcoming the recommendations of Mol et al. to use a TEMPO catalyst and I do not see how Fremont et al. could have led us to our invention involving the use of peroxide with transition metals in back-flush at relatively low concentrations, or the use of hypochlorite in back-flush at relatively low concentrations.
13. Schuchardt describes the treatment of waste water issuing from the production of polyether polyols. Polyether polyols as described by Schuchardt are polyethoxylated glycerols of e.g. the formula $A-OCH_2-CH(O-A)-CH_2O-A$, wherein $A = (CH_2-CH_2O)_n-H$, with n in the order of 40 in view of their molar weight of about 5,000 as mentioned in the Examples of Schuchardt. These are synthetic, flexible, water-soluble polymers having a very limited number (3 on 5,000 Da) of hydroxyl groups. They have nothing to do with polyphenols, which are plant-derived, natural aromatic products such as catechins, carrying several hydroxyl groups on rather small molecules. Contrary to the polyether polyols, the polyphenols have limited solubility and are poorly degradable. Moreover, the treatment of Schuchardt takes place in dilute solution, while the contaminants to be removed in our process are present in the cakes which result from the filtering of beverages and which obstruct the membrane filters. Thus the teaching of Schuchardt is of no use in solving our problem.
14. I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001

of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Dated: Zeist July 7, 2010
(place) (date)

Signature:

Jan M. Jettin

A handwritten signature in black ink, appearing to be 'J. M. Jettin', written over the printed name 'Jan M. Jettin'.